

### PROCESS FOR MANUFACTURING ETHYLENE OXIDE

The present invention relates to a process for manufacturing ethylene oxide by the catalytic oxidation reaction of ethylene.

The catalytic oxidation reaction of ethylene by molecular oxygen leading to the formation of ethylene oxide is known to be strongly exothermic. It is often carried out in a tube reactor, in particular a vertical multitubular shell exchanger type reactor or a vertical shell-and-tube exchanger type reactor. In general, the tube reactor comprises three successive and adjacent chambers traversed by a reactive gas current comprising ethylene and molecular oxygen: an inlet chamber of the reactive gas current, then a central chamber where the ethylene oxide is formed in a gas current resulting from the catalytic oxidation reaction and an outlet chamber of the resulting gas current. The central chamber comprises generally a bundle of reaction tubes immersed in a heat exchange fluid and filled with a solid silver-based catalyst. The reactive gas current passes to the interior of the reaction tubes and, by contact with the catalyst, leads to the formation of ethylene oxide in the gas current resulting from the reaction. Each reaction tube comprises an inlet issuing into the inlet chamber and an outlet issuing into the outlet chamber. In each of the reaction tubes, three successive zones from the inlet to the outlet of the tubes are generally found, that is to say in the flow direction of the gas current, namely a pre-heating zone situated towards the inlet of the tubes, then a reaction zone and a quenching or cooling zone situated towards the outlet of the tubes.

The desired product of the catalytic oxidation reaction of ethylene is ethylene oxide. However, non-desired secondary reactions may take place, such as complete oxidation of the ethylene and ethylene oxide into carbon dioxide and water, isomerisation of the ethylene oxide into acetaldehyde and the secondary oxidation of

ethylene into formaldehyde. Said secondary reactions contribute to lowering the selectivity of the catalytic oxidation reaction of the ethylene to ethylene oxide.

Several problems arise simultaneously in the manufacture of ethylene oxide. The most serious problems are linked to the strongly exothermic character of the catalytic oxidation reaction of ethylene to ethylene oxide and to the control of the temperature of the reaction, in particular the whole length of the reaction tubes, from the entry of the reactive gas mixture into the tube reactor up to the exit of the gaseous mixture resulting from the reaction. One of the major risks of the process is the formation of hot spots leading to reaction runaways, known generally by the term "post-combustion", and to the formation of carbon dioxide, carbon monoxide and aldehydes such as formaldehyde and acetaldehyde, some of said secondary products being particularly difficult to separate subsequently from the ethylene oxide. An irregular reaction temperature profile, poorly controlled and in particular increasing along the whole length of the reaction tubes, may lead not only to hot spots, but also to an excessive final temperature. The hot spots and an excessive final temperature affect the selectivity of the reaction to ethylene oxide. In addition, a locally high temperature and an excessive final temperature may be such that they attain a value corresponding to the maximum flammability temperature of the gaseous mixture, and thus cause an explosion.

Solutions have been proposed for partially resolving some of said problems through methods of various degrees of complexity. There is proposed in Australian patent AU 211 242 a process for manufacturing ethylene oxide in a tube reactor consisting of conventional reaction tubes which comprise an inlet zone filled with inert particles such as spheres of alumina and an empty outlet zone. Between said two zones, the reaction tubes comprise a reaction zone filled with a silver-based supported catalyst the concentration of which rises between the inlet and the outlet of said zone. As a result, the catalytic activity increases along the reaction tubes, from the inlet up to the outlet of the tubes, in the flow direction of the reactive gas current.

There is proposed in American patent US 5,292,904 a process for manufacturing ethylene oxide in a tube reactor consisting of conventional reaction tubes which comprise a pre-heating zone situated towards the inlet of the tubes and a cooling zone situated towards the outlet of the tubes, said two zones being filled with an inert refractory product such as a refractory alumina.

There is proposed in International patent application WO 02/26370 a catalytic

reaction process in a tube reactor consisting of conventional reaction tubes which comprise an upstream portion and/or a downstream portion situated respectively towards the inlet and the outlet of the tubes, said portions containing a heat exchange insert mainly in the form of rods and having a length equal to 1 to 20 % of the total

5 length of the reaction tube. When the process is used for the manufacture of ethylene oxide, it is stated that the upstream and downstream portions of the reaction tubes contain the insert, and that the insert contained in the upstream portion may have a length equal to 1 to 10 % of the total length of the reaction tube, while the insert contained in the downstream portion may have a length twice that contained in the  
10 upstream portion. However, it is noticed that in all cases the catalyst occupies solely the central portion of the reaction tubes and that a not inconsiderable portion of the tubes is thus filled with inert solid materials intended to promote solely the heat exchanges. Thus, a relatively great portion of the conventional reaction tubes is not reserved for the production of ethylene oxide and as a result affects the production of ethylene oxide per  
15 unit of internal tube volume available in the reactor.

International patent application WO 03/01149 describes a tubular reactor used for exothermic chemical conversions of organic compounds. The tubular reactor comprises reaction tubes filled with a catalyst and through which a reactive gas current flows.

Each reaction tube comprises a sequence of zones such that each downstream zone has a  
20 smaller or preferably larger cross-section than the contiguous upstream zone. However, as illustrated in the Figures, the cross-section of the reaction tubes only increases from the prior upstream zone in tubular reactors which are particularly used for manufacturing maleic anhydride and also used for manufacturing other organic compounds such as phthalic anhydride, ethylene oxide, acrylic acid, vinyl acetate or  
25 ethylene dichloride.

German patent application DE 29 29 300 describes a catalytic reactor, for use in carrying out endothermic or exothermic reactions, through which a reactant fluid is flowed, and comprising reaction tubes filled with catalyst material, which are in thermal contact with a heat-emitting or heat-absorbing fluid, and characterized in that the cross-  
30 section surface area of the reaction tubes is varied, along with the direction of flow of the reacting fluid, depending upon the quantity of heat required for completion of a given reaction, or the quantity of heat released on the course of a reaction. However, as illustrated in Figures 1 and 4, the cross-section surface area of the reaction tubes firstly

decreases and then increases along with the direction of flow of the reacting fluid, while in Figure 2 the cross-section surface area firstly increases and then decreases, in Figure 3 the cross-section surface area increases for some reaction tubes and decreases for the other reaction tubes in the reactor, and in Figure 5 the cross-section surface area decreases. The reactors described by the German patent application are proposed to be used in methanol or ammonia synthesis. The reactor shown in Figure 2 is specifically used for methanol synthesis which is an exothermic reaction.

The process of the present invention is intended to resolve the technical problems described above. It is intended in particular to increase the selectivity of the catalytic oxidation reaction of ethylene to ethylene oxide and the production of ethylene oxide per unit of internal tube volume available in the reactor, and simultaneously to improve the safety of the process in particular as regards the risks of reaction runaway and explosion, by controlling in particular the profile of the temperature of the reaction the whole length of the reaction tubes.

The present invention relates to a process for manufacturing ethylene oxide by the catalytic oxidation reaction of ethylene by molecular oxygen in a tube reactor comprising three successive and adjacent chambers traversed by a reactive gas current comprising ethylene and molecular oxygen, an inlet chamber of the reactive gas current, then a central chamber forming a gas current resulting from the reaction and comprising the ethylene oxide, and an outlet chamber of the resulting gas current, the central chamber comprising a bundle of reaction tubes immersed in a heat exchange fluid and filled with a solid silver-based catalyst in contact with which the reactive gas current forms the ethylene oxide, each reaction tube possessing an inlet issuing into the inlet chamber and an outlet issuing into the outlet chamber, the process being characterised in that the area of the internal cross-section of the reaction tubes decreases between the inlet and the outlet of the tubes over at least a portion of the length of the tubes and remains constant over any remaining portion.

Figure 1 represents diagrammatically a tube reactor comprising reaction tubes as used in the process of the invention.

Figures 2a, 2b, 3, 4a and 4b represent diagrammatically various reaction tubes as used in the process of the invention.

Figure 5 represents a graph linking, on the ordinate, the temperature of the reactive gas current (measured in degrees Celsius) with, on the abscissa, the length of

the reaction tube (measured in metres) from the inlet of the tube, said graph being drawn according to the conditions of Example 1.

Figure 6 represents a graph linking, on the ordinate, the selectivity (S) of the reaction to ethylene oxide (expressed in %) to, on the abscissa, the production (P) of ethylene oxide (expressed in tonnes of ethylene oxide per day) in the conditions of Examples 1 and 2 and of Comparative Example 3.

According to the invention, it was found that it is possible to obtain a relatively stable reaction temperature profile the whole length of the reaction tubes, to avoid reaction runaways and to reduce significantly the final temperature of the reaction, while at the same time improving the selectivity and the output of the reacting to ethylene oxide, in particular when from the inlet up to the outlet of the reaction tubes (i.e. in the flow direction of the reactive gas current) the area of the internal cross-section of the tubes decreases over the whole length of the tubes, or decreases over at least a portion of the length of the tubes and remains constant over the remaining portion. In particular, the reaction tubes have a shape so that the area of the internal cross-section of the tubes do not increase over any portion of the tubes in the flow direction of the reactive gas current. The area may decrease continuously or, preferably, discontinuously, in particular by stages. Furthermore, all the reaction tubes present in the tube reactor preferably have an internal cross-section as previously described according to the present invention.

The effects sought by the present invention are particularly attractive when the area of the internal cross-section (A1) at the inlet of the reaction tubes is from 1.5 to 12 times, preferably from 2 to 10 times, in particular from 3 to 9 times greater than the area of the internal cross-section (A2) at the outlet of said tubes.

The effects sought may, in addition, be particularly remarkable in the following conditions. When the decrease in the area of the internal cross-section of the reaction tubes is effected once only over the length of the tubes, either continuously over a portion of the length of the tubes, or discontinuously, more particularly by a stage, it may be effected at the latest (in the flow direction of the reactive gas current) before the last fifth of the length of the tubes (situated towards the outlet), preferably before the last quarter, in particular before the last third, more particularly before the last half of the length of the tubes (situated towards the outlet), or else at the earliest not before the first third of the length of the tubes (situated towards the inlet). When the decrease in

the area of the internal cross-section of the reaction tubes is effected two or more successive times over the length of the tubes, either continuously over two or more portions of the length of the tubes, or discontinuously, more particularly in two or more successive stages, it may be effected for the first time at the latest (in the flow direction of the reactive gas current) before the last fifth of the length of the tubes (situated towards the outlet), preferably before the last quarter, in particular before the last third, more particularly before the last half of the length of the tubes (situated towards the outlet), or else at the earliest not before the first third of the length of the tubes (situated towards the inlet), e.g. not before the first 5/12 of the length of the tubes (situated towards the inlet).

For example, the reaction tubes may have a length (L) of from 6 to 20 m, preferably from 8 to 15 m, an area of the internal cross-section (A1) at the inlet of the tubes of from 12 to 80 cm<sup>2</sup>, preferably from 16 to 63 cm<sup>2</sup>, and an area of the internal cross-section (A2) at the outlet of the tubes of less than A1 and ranging from 1.2 to 16 cm<sup>2</sup>, preferably from 1.8 to 12 cm<sup>2</sup>.

The tube reactor is generally of the vertical shell-and-tube exchanger type, that is to say comprising a vertical bundle of reaction tubes. By bundle of reaction tubes is meant generally an assembly of mutually identical and parallel tubes. According to a practical form of the invention, the reaction tubes may have a cylindrical shape and exhibit a circular internal cross-section whose internal diameter (Di) decreases between the inlet and the outlet of the tubes over at least a portion of the length of the tubes and remains constant over any remaining portion. Thus, it was found that from the inlet up to the outlet of the reaction tubes the internal diameter (Di) of the tubes may decrease over the whole length of the tubes, or may decrease over at least a portion of the length of the tubes and remain constant over the remaining portion. The internal diameter (Di) may decrease continuously or discontinuously, in particular by stages, from the inlet up to the outlet of the tubes. Good results are obtained in particular when the internal diameter (D1i) at the inlet of the reaction tubes is from 1.2 to 3.5 times, preferably from 1.4 to 3.1 times, more particularly from 1.7 to 3 times higher than the internal diameter (D2i) at the outlet of said tubes.

Remarkable results may also be obtained in the following circumstances. When the internal diameter (Di) of the reaction tubes decreases once only over the length of the tubes, either continuously over a portion of the length of the tubes or

discontinuously, in particular by a stage, the decrease of  $D_i$  may be effected at the latest (in the flow direction of the reactive gas current) before the last fifth of the length of the tubes (situated towards the outlet), preferably before the last quarter, in particular before the last third, more particularly before the last half of the length of the tubes (situated towards the outlet), or else at the earliest not before the first third of the length of the tubes (situated towards the inlet). When the internal diameter ( $D_i$ ) of the reaction tubes decreases two or more successive times over the length of the tubes, either continuously over two or more portions of the length of the tubes or discontinuously, in particular by two or more stages, the decrease of  $D_i$  may be effected for the first time at the latest (in the flow direction of the reactive gas current) before the last fifth of the length of the tubes (situated towards the outlet), preferably before the last quarter, in particular before the last third, more particularly before the last half of the length of the tubes (situated towards the outlet), or else at the earliest not before the first third of the length of the tubes (situated towards the inlet), e.g. not before the first 5/12 of the length of the tubes (situated towards the inlet).

For example, the reaction tubes of cylindrical shape may have a length ( $L$ ) of from 6 to 20 m, preferably from 8 to 15 m, an internal diameter ( $D_i$ ) which, according to the invention, decreases between the inlet and the outlet of the tubes and which may be chosen in a range of from 12 to 100 mm, preferably from 15 to 90 mm. In addition, the reaction tubes may have an internal diameter ( $D_{1i}$ ) at the inlet of the tubes which may be chosen in a range of from 38 to 100 mm, preferably from 45 to 90 mm, and an internal diameter ( $D_{2i}$ ) at the outlet of the tubes which is less than  $D_{1i}$  and which may be chosen in a range of from 12 to 45 mm, preferably from 15 to 40 mm.

According to the invention, the reaction tubes have an internal cross-section whose area decreases between the inlet and the outlet of the tubes. They may, in addition, have a wall whose thickness is constant, or on the contrary varies, for example decreases or increases from the inlet up to the outlet of the tubes (in the flow direction of the reactive gas current). It is possible in particular to use reaction tubes of cylindrical shape which have an internal diameter ( $D_i$ ) which decreases from the inlet up to the outlet of the tubes, for example continuously or discontinuously, in particular by stages, as described previously according to the invention, and which may, in addition, have an external diameter ( $D_e$ ) which is constant between the inlet and the outlet of the tubes and equal in particular to the external diameter ( $D_{1e}$ ) at the inlet of said tubes. In this

case, it was found in a remarkable manner that the resulting enlargement of the wall of the reaction tubes from the inlet up to the outlet of the tubes does not affect, or only in an insignificant manner, the effects sought by the process of the invention.

The solid silver-based catalyst used in the present invention may be chosen from among the silver-based supported catalysts capable of catalysing the oxidation of ethylene to ethylene oxide with the aid of molecular oxygen. The catalyst may be chosen from among catalysts comprising mainly of metallic silver deposited on a porous refractory solid support. The support may be chosen from among refractory products of natural, artificial or synthetic origin, preferably from among those having a macro-porous structure, more particularly having a specific surface area (B.E.T.) of less than 20 m<sup>2</sup>/g, in particular of from 0.01 to 10 m<sup>2</sup>/g, and an apparent porosity of more than 20 % by volume, more particularly of from 30 to 70 % by volume. The most appropriate supports may be those which comprise of siliceous and/or aluminous products (based on silica and/or alumina respectively). For example, the support may be chosen from among oxides of aluminium (in particular those known under the trade reference "Alundum"®), charcoal, pumice stone, magnesia, zirconium, kieselguhr, fuller's earth, silicon carbide, porous agglomerates containing silicon and/or silicon carbide, clays, natural, artificial or synthetic zeolites, metal oxide gel-based materials containing oxides of heavy metals such as molybdenum or tungsten, and ceramic products. Aluminous products are preferred, in particular those containing alumina of the alpha type, having in particular a specific surface area (B.E.T.) of from 0.15 to 0.6 m<sup>2</sup>/g and an apparent porosity of from 46 to 52 % by volume. The B.E.T. method used to determine the specific surface area is described in J. Am. Chem. Soc., 60, 309 – 16 (1938).

The catalyst may contain from 1 to 20 %, preferably from 2 to 16 % by weight of silver. It may in addition contain at least one metallic promoter agent, in particular chosen from among the alkaline metals, alkaline-earth metals such as calcium or barium, and other metals such as thallium, antimony, tin or rhenium. The catalyst may come in the form of particles having in particular a mean diameter at least equal to 1 or 2 mm and at most equal to half of the narrowest internal diameter of the reaction tubes employed, in particular a mean diameter chosen from a range of from 1.5 to 15 mm, preferably from 4 to 8 mm, for example in the form of spherical or hemispherical particles, rings, pellets or granules. The catalyst may be prepared according to various processes such as those described in the American patents US 3,043,854, US 3,207,700,



US 3,575,888, US 3,702,259 and US 3,725,307, or in the European patent EP 0 266 015.

One of the advantages of the present invention is being able to use reaction tubes containing the catalyst over the whole or at least over almost the whole (that is to say  
5 more than 95 %) of the length of the tubes, from the inlet up to the outlet of the tubes, and more particularly in the zone situated towards the outlet. Only one portion, generally at most equal to 5% of the length, situated towards the outlet, may be occupied by a device for supporting the catalyst charge, such as a grille or spring).

Hence, thanks to the particular configuration of the reaction tubes according to the  
10 present invention, a maximum catalyst charge may be employed for the internal tube volume available in the reactor, and said charge is capable of being, in addition, active for the production of ethylene oxide. Said advantageous results are, in addition, obtained while at the same time maintaining a high selectivity of the reaction to ethylene oxide and supplying in particular a relatively stable reaction temperature  
15 profile over the whole length of the tubes. It may be possible, however, if it is so desired, to insert into the reaction tubes inert solid materials, or preferably, where applicable, to mix the catalyst with said materials. The inert solid materials may be optionally chosen from among inert particles or solid and in particular hollow inserts, for example of metal or of metal alloy, or of inert refractory product used in particular  
20 as a solid inert filling product, for example in the form of powdery, spherical or hemispherical particles, rings, pellets or granules. The inert refractory products optionally used may be of an identical or different nature to those of the supports present in the catalyst. They may be chosen from among the catalyst supports, in particular those mentioned previously, and from among refractory products having in  
25 particular a small B.E.T. specific surface area, preferably of less than 0.1, more particularly less than 0.05, in particular less than 0.01 m<sup>2</sup>/g. The refractory products with a small B.E.T. specific surface area may be chosen from among silica, alumina, silicon carbide, alumina and silica mixtures optionally modified by alkaline or alkaline-earth metals, ceramic products, glass-type materials such as sodium polysilicates  
30 containing more particularly a stoichiometric excess of silica.

The process for manufacturing ethylene oxide employs molecular oxygen, which may be used in the form of pure molecular oxygen, for example with an oxygen purity equal to or more than 95 % by volume, or in the form of air. The reactive gas current

which traverses the tube reactor may consist of a gaseous mixture of ethylene, molecular oxygen and optionally one or more other gases chosen from among carbon dioxide, nitrogen, argon, methane, ethane and at least one reaction inhibitor or moderator chosen in particular from among halogenated hydrocarbons such as ethyl chloride, vinyl chloride or 1,2-dichloroethane. In the reactive gas current, the concentration of ethylene is generally as high as possible, more particularly equal to or less than 40 % by volume, and it is in particular chosen from a range of from 15 to 35 % by volume. The concentration of molecular oxygen in the reactive gas current may be chosen from a range of 3 to 20 %, preferably of 4 to 10 % by volume. The concentration of carbon dioxide in the reactive gas current is generally less than or equal to 10 % by volume, and may be chosen from a range of from 4 to 8 % by volume. Methane and/or nitrogen may be used as diluents in the reactive gas current in order more particularly to reduce the flammability range of the gaseous mixture and to remove it into a zone not used. Thus methane and/or nitrogen may be present in the reactive gas current in a concentration as high as possible. For example, the reactive gas current may contain by volume from 1 to 40 % of ethylene, from 3 to 12 % of molecular oxygen, from 0 to 10 % of carbon dioxide, from 0 to 3 % of ethane, from 0.3 to 50 parts by volume per million (vpm) of a reaction inhibitor or moderator of the halogenated hydrocarbon type, the remainder being argon and/or nitrogen and/or methane. The absolute pressure of the reactive gas current in the tube reactor may be chosen in a range of from 0.1 to 4 MPa, preferably from 1 to 3 MPa. The volume space hour velocity (VSHV) of the reactive gas current in the reaction tubes may be chosen in a range of from 1000 to 10 000 h<sup>-1</sup> (m<sup>3</sup> per m<sup>3</sup>.h of catalyst), preferably from 2000 to 8000 h<sup>-1</sup>, measured in standard temperature and pressure conditions.

The reactive gas current may with advantage be pre-heated to a temperature of from 100 to 200 °C, preferably from 140 to 190 °C. The temperature of the reactive gas current in the reaction tubes may be chosen in a range of from 140 to 350 °C, preferably from 180 to 300 °C, more particularly from 190 to 280 °C. Owing to the process of the invention, the temperature of the reactive gas current at the inlet of the reaction tubes may rise very rapidly or as it were instantaneously to a temperature equal to or more than 210 °C. It may then continue to increase, but far more moderately, and attain a maximum temperature of at most equal to 270 °C, preferably at most equal to 265 °C, more particularly at most equal to 260 °C, in particular over a portion of the length of

the tubes capable of extending from the first quarter to the fourth fifth, preferably from the first half to the third quarter of the length of the tubes in the flow direction of the reactive gas current. At the outlet of the reaction tubes, the temperature of the gas current resulting from the reaction may remain at said maximum temperature or,  
5 preferably, may decrease to a temperature equal to or less than 250 °C, preferably equal to or less than 240 °C, more particularly equal to or less than 230 °C, for example in a range of from 180 to 250 °C, preferably from 190 to 240 °C, more particularly from 200 to 230 °C.

It is particularly advantageous to note that, owing to the process of the invention,  
10 the exchange of heat along the reaction tubes makes it possible to combine a relatively stable reaction temperature profile and a maximum quantity of catalyst used in optimum activity conditions (the whole length of the tubes and more particularly in the zone situated towards the outlet of the tubes) per unit of internal tube volume available in the reactor. Said combination makes it possible to prevent a relatively great portion of the  
15 reaction tubes being sacrificed to something other than the production of ethylene oxide and the maintenance of the catalyst charge in the tubes, more particularly by an absence of the catalyst, namely with the sole aim of controlling the heat exchanges and preventing hot spots. One of the major advantages of the process of the invention may further come from the fact that the temperature of the gas current resulting from the  
20 reacting at the outlet of the reaction tubes may be substantially reduced by at least 5 °C, for example by at least 10 °C, compared with the conventional processes. The result of said substantial reduction in the temperature is that for any other furthermore equal condition, such as an identical concentration of molecular oxygen in the reactive gas current, the limits of flammability of said current may be distanced accordingly and may  
25 thus permit a far safer process to be provided without in so doing sacrificing the yield and the selectivity of the reaction to ethylene oxide.

The bundle of reaction tubes is immersed in a heat exchange fluid which may be chosen in particular from among organic heat carrying fluids and water superheated under pressure (that is to say water at saturation temperature). The organic heat carrying  
30 fluids may be mixtures of oils or hydrocarbons such as linear or branched alkanes having in particular a boiling point higher than the maximum reaction temperature. It is possible to use the organic heat carrying fluids at a relative pressure of from 100 to 1500 kPa, preferably from 200 to 800 kPa, more particularly from 200 to 600 kPa. The

organic heat carrying fluids may be chosen in particular from "Isopar"® of Exxon, "Therminol"® of Monsanto and "Dowtherm"® of Dow Chemicals. They may be used according to a process and a heat exchange apparatus as described in European patent application EP 0 821 678, in particular in Figure 1 or 2, or else in American patent US 4,759,313. The heat exchange fluid may also be water superheated under pressure, in particular used at a relative pressure of from 1500 to 8000 kPa. In this case, the superheated water may be used according to a process and a heat exchange apparatus as described in American patent US 5,292,904. The temperature of the heat exchange fluid at the outlet of the tube reactor generally lies between 210 and 300 °C, preferably between 220 and 280 °C, more particularly between 210 and 280 °C. The temperature of the heat exchange fluid at the inlet of the tube reactor generally lies between 120 and 250 °C, preferably between 130 and 240 °C, more particularly between 130 and 230 °C.

The process of the invention may with advantage be carried out continuously, more particularly by utilising continuously the reactive gas current which traverses successively and continuously the three chambers of the tube reactor and by recovering continuously at the outlet of the reactor the gas current resulting from the reaction and containing the ethylene oxide.

Figure 1 is a diagrammatic representation of a tube reactor as used in the process of the invention. The tube reactor is of the vertical shell-and-tube exchanger type. The reactor contains three successive and adjacent chambers: an inlet chamber (1), then a central chamber (2) and an outlet chamber (3). There issues into the inlet chamber (1) a pipe (4) for the feeding of a reactive gas current containing ethylene and molecular oxygen. The central chamber (2) comprises a bundle of reaction tubes (5) parallel and identical to one another, and preferably cylindrical, each tube (5) containing in inlet (6) issuing into the inlet chamber (1) and an outlet (7) issuing into the outlet chamber (3). The reaction tubes (5) are filled with a solid silver-based catalyst (8) (shown tinted grey) over the whole or almost the whole of the length of the tubes (with the exception of a device for supporting the catalyst charge in the tube, such as a grille or a spring, not shown in Figure 1). The area of the internal cross-section of each reaction tube (5) decreases discontinuously between the inlet (6) and the outlet (7) of the tubes, by three successive stages (9), so that each reaction tube (5) is composed of four successive and contiguous tubular sections (10), each having an increasingly reduced internal cross-sectional area from the inlet (6) to the outlet (7). The reaction tubes (5) are immersed in

a heat exchange fluid (11) which is introduced into the central chamber (2) through a pipe (12) for the feeding of fluid and which is drawn off from the central chamber (2) through a discharge pipe (13). The outlet chamber (3) is provided with a pipe (14) for discharge of the gaseous current resulting from the reaction and containing the ethylene oxide.

Figures 2a and 2b are diagrammatic representations of the reaction tubes (5) capable of being used in the tube reactor shown in Figure 1 and enabling the process of the invention to be carried out. The elements of Figures 2a and 2b identical to those shown in Figure 1 are marked with the same numerical references. Figure 2a represents diagrammatically a reaction tube (5) which is provided with an inlet (6) and an outlet (7), and which has an internal cross-sectional area which decreases continuously from the inlet (6) to the outlet (7). Figure 2b represents diagrammatically a reaction tube (5) provided with an inlet (6) and an outlet (7). The area of the internal cross-section of the reaction tube (5) decreases continuously over a portion (15) of the length of the tube, and remains constant over the remaining upstream portion (16) situated towards the inlet (6) and over the remaining downstream portion (17) situated towards the outlet (7). The reaction tubes (5) as represented in Figures 2a and 2b are shown empty and without the catalyst (8) as represented in Figure 1.

Figure 3 is a diagrammatic representation of a reaction tube (5) capable of being used in the tube reactor shown in Figure 1 according to the process of the invention. The elements of Figure 3 identical to those shown in Figure 1 are marked with the same numerical references. The reaction tube (5) is provided with an inlet (6) and an outlet (7). The area of the internal cross-section of the reaction tube (5) decreases discontinuously between the inlet (6) and the outlet (7), by two successive stages (9), so that the reaction tube (5) is composed of three successive and contiguous tubular sections (10), each having an increasingly reduced internal cross-sectional area from the inlet (6) to the outlet (7). The reaction tube (5) as shown in Figure 3 is shown empty and without the catalyst (8) as represented in Figure 1.

Figures 4a and 4b are diagrammatic representations of the reaction tubes (5) capable of being used in the tube reactor shown in Figure 1 and enabling the process of the invention to be carried out. The elements of Figures 4a and 4b identical to those shown in Figure 1 are marked with the same numerical references. Figure 4a represents diagrammatically a reaction tube (5) of cylindrical shape which is provided with an

inlet (6) and an outlet (7). The area of the circular internal cross-section of the reaction tube decreases discontinuously between the inlet (6) and the outlet (7), by two successive stages (9), so that the reaction tube (5) is composed of three successive and contiguous cylindrical tubular sections (10), each having an increasingly reduced internal diameter ( $D_i$ ) from the inlet (6) to the outlet (7). The reaction tube (5) possesses an external diameter ( $D_e$ ) which remains constant between the inlet (6) and the outlet (7). The reaction tube (5) may be in practice composed of three cylindrical and coaxial tubes ( $10_A$ ,  $10_B$  and  $10_C$ ) inserted into one another, so that in particular the external surface of the tube  $10_B$  is contiguous with the internal surface of the tube  $10_A$ , and that the external surface of the tube  $10_C$  is contiguous with the internal surface of the tube  $10_B$ . Figure 4b represents diagrammatically a reaction tube (5) of cylindrical shape which is provided with an inlet (6) and an outlet (7). The reaction tube (5) possesses an internal diameter ( $D_i$ ) which decreases continuously over a portion (15) of the length of the tube, and which remains constant over the remaining upstream portion (16) situated towards the inlet (6) and over the remaining downstream portion (17) situated towards the outlet (7). The reaction tube (5) possesses an external diameter ( $D_e$ ) which remains constant between the inlet (6) and the outlet (7). The reaction tube (5) may be in practice composed of two cylindrical and coaxial tubes ( $16_A$  and  $17_A$ ) inserted into one another, so that in particular the external surface of the tube ( $17_A$ ) is contiguous with the internal surface of the tube ( $16_A$ ). The tube ( $17_A$ ) is prolonged and contiguous with a tube ( $15_A$ ) coaxial with the two tubes ( $16_A$  and  $17_A$ ). The tube ( $15_A$ ) has a cylindrical external wall whose surface is contiguous with the internal surface of the tube ( $16_A$ ), and a revolving truncated internal wall whose large base contiguous with the tube ( $17_A$ ) has a diameter identical to the internal diameter of the tube ( $17_A$ ) and whose small base has a diameter identical to the internal diameter ( $D_i$ ) of the tube ( $16_A$ ). The reaction tubes (5) as shown in Figures 4a and 4b are shown empty and without the catalyst (8) as represented in Figure 1.

The process of the present invention offers in particular the following advantages:

- a substantially increased selectivity of the reaction to ethylene oxide for one and the same level of production of ethylene oxide, for example of at least 3 points (expressed in %);
- a clearly increased production of ethylene oxide by unit of internal tube volume available in a tube reactor;

- a maximum charge of active catalyst in the production of ethylene oxide per unit of internal tube volume available in a tube reactor;
- a relatively stable reaction temperature profile the whole length of the reaction tubes;
- 5 - a substantially reduced temperature at the outlet of the reaction tubes compared with that of the conventional processes;
- a safer process for manufacturing ethylene oxide by virtue of operating conditions which are more removed from the flammability conditions of the gas current;
- a substantial decrease in the quantity of carbon dioxide produced compared with that of ethylene oxide, and a marked reduction in the discharges of carbon dioxide into the environment.

The selectivity of the reaction to ethylene oxide (expressed in %) may be calculated according to the following equation:

$$15 \quad (1) \quad \text{Selectivity} = 100 \times (\text{molar production of ethylene oxide}) / (\text{molar consumption of ethylene})$$

The following examples illustrate the present invention.

#### 20 **Example 1**

The manufacture of ethylene oxide was carried out continuously in a tube reactor as shown in Figure 1, comprising an inlet chamber (1), a central chamber (2) and an outlet chamber (3). The central chamber (2) comprised a bundle of 3709 cylindrical reaction tubes, identical and parallel to one another. Each reaction tube (5), as shown diagrammatically in Figure 3, comprised two successive stages (9), such that the tube (5) was composed of three successive and contiguous cylindrical tubular sections (10), each having a length (L) and an internal diameter (Di) decreasing between the inlet (6) and the outlet (7). The length (L) and the internal diameter (Di) of the three sections (10) had successively between the inlet (6) and the outlet (7) of the tubes the following values: L = 5 m and Di = 51.2 mm; L = 5 m and Di = 38.4 mm; L = 2 m and Di = 25.6 mm. The reaction tubes (5) were filled with a silver-based supported catalyst, in an equal manner between one another and over almost the whole (96%) of their length (only a last portion 0.5 m in length situated just before the outlet (7) being occupied by a

spring for supporting the catalyst in the tube). The catalyst was a catalyst containing 14.7 % by weight of silver supported on alumina. The total volume of the catalyst introduced into the reaction tubes of the reactor is about 62.5 m<sup>3</sup>.

There was introduced continuously into the tube reactor a reactive gas current containing by volume 28.2 % of ethylene, 6.5 % of molecular oxygen, 5 % of carbon dioxide, 4.7 % of nitrogen, 5.5 % of argon, 0.3 % of ethane, 4.8 vpm of ethyl chloride, the remainder being methane, at a flow rate of 270.8 tonnes/hour, at an absolute pressure of 2.06 MPa, the reactive gas current being pre-heated to about 150 °C. Replenishments with fresh constituents of the reactive gas current, more particularly with fresh ethylene and oxygen, were carried out continuously to enable the composition of said current to be kept constant during the production. The bundle of reaction tubes was immersed in water superheated to 210 °C (at saturation temperature). The temperature of the reactive gas current was measured along the reaction tubes, which made it possible, according to the graph shown in Figure 5, to draw a curve (1) plotting the temperature of the gas current as a function of the length of the tube (S) starting from the inlet (6).

Five tests were conducted in said conditions, the rates of introduction of fresh constituents of the reactive gas current, more particularly of fresh ethylene and oxygen, being changed for each of them in order to obtain for each test a production (P) of ethylene oxide (expressed in tonnes of ethylene oxide per day) and for each production (P) thus obtained the selectivity (S) of the reaction to ethylene oxide (expressed in %) was calculated according to equation (1) mentioned above. The results of said tests were listed in Table 1 and enabled a curve (1) to be drawn according to the graph shown in Figure 6 linking the selectivity (S) to the production (P) of ethylene oxide.



**Table 1:** Selectivity (S) as a function of the production (P) of ethylene oxide

Example 1	Test	Selectivity (S) (%)	Production (P) (t/d)
	1	83.2	256
	2	82.1	275
	3	81.0	290
	4	79.8	302
	5	78.5	314

**Example 2**

Exactly the same procedure was adopted as in Example 1, except that the tube reactor comprised a bundle of 2760 cylindrical reaction tubes (5), identical and parallel to one another, and that each tube (5) as shown in Figure 3 comprised two successive stages (9), so that the tube was composed of three successive and contiguous cylindrical tubular sections (10), each having a length (L) and an internal diameter (Di) decreasing between the inlet (6) and the outlet (7). The length (L) and the internal diameter (Di) of the three sections (10) had successively between the inlet (6) and the outlet (7) of the tubes the following values: L = 5 m and Di = 64.0 mm; L = 5 m and Di = 38.4 mm; L = 2 m and Di = 25.6 mm. The reaction tubes were filled with the silver-based catalyst, as in Example 1, in an equal manner between one another and over almost the whole (96 %) of their length. The total volume of the catalyst introduced into the reaction tubes of the reactor was substantially identical to that of Example 1.

Three tests were conducted in said conditions, the rates of introduction of fresh constituents of the reactive gas current, more particularly of fresh ethylene and oxygen, being changed for each of them in order to obtain for each test a production (P) of ethylene oxide (expressed in tonnes of ethylene oxide per day) and for each production (P) thus obtained the selectivity (S) of the reaction to ethylene oxide (expressed in %) was calculated according to equation (1) mentioned above. The results of said tests were listed in Table 2 and enabled a curve (2) to be drawn according to the graph shown in Figure 6 linking the selectivity (S) to the production (P) of ethylene oxide.

**Table 2:** Selectivity (S) as a function of the production (P) of ethylene oxide

Example 2	Test	Selectivity (S) (%)	Production (P) (t/d)
	1	81.7	277
	2	80.4	299
	3	78.9	315

**Example 3 (comparative)**

5 Exactly the same procedure was adopted as in Example 1, except that the tube reactor comprised a bundle of 4750 cylindrical reaction tubes (5), identical and parallel to one another, and that each tube (5) had a conventional shape and possesses in particular an internal diameter ( $D_i$ ) which was constant between the inlet (6) and the outlet (7) of the tubes and which was equal to 38.7 mm, and a length (L) of 12 m. The  
 10 reaction tubes were filled with the silver-based catalyst, as in Example 1, in an equal manner between them and over almost the whole (96 %) of their length. The total volume of catalyst introduced into the reaction tubes of the reactor was substantially identical to that of Example 1.

The temperature of the reactive gas current was measured along the reaction  
 15 tubes, which enabled a curve (2) to be drawn according to the graph shown in Figure 5 plotting the temperature of the gas current as a function of the length of the tube (5) starting from the inlet (6).

Five comparative tests were conducted in said conditions, the rates of introduction of fresh constituents of the reactive gas current, more particularly of fresh ethylene and  
 20 oxygen, being changed for each of them in order to obtain for each test a production (P) of ethylene oxide (expressed in tonnes of ethylene oxide per day) and for each production (P) thus obtained the selectivity (S) of the reacting to ethylene oxide (expressed in %) was calculated according to equation (1) mentioned above. The results of said tests were listed in Table 3 and enabled a curve (3) to be drawn according to the  
 25 graph shown in Figure 6 linking the selectivity (S) to the production (P) of ethylene oxide.

**Table 3: Selectivity (S) as a function of the production (P) of ethylene oxide**

Example 3 (comparative)	Test	Selectivity (S) (%)	Production (P) (t/d)
	1	83.8	235
	2	82.8	248
	3	81.8	257
	4	80.8	266
	5	79.7	275

5 An analysis of the results given in Tables 1, 2 and 3 and in the graphs of Figures 5 and 6 shows that:

- (a) according to the process of the invention, the reaction temperature profile along the tubes was relatively stable between the inlet and the outlet of the tubes (curve (1) of Figure 5), compared with the temperature profile obtained with conventional reaction tubes (curve (2) of Figure 5); thus according to the invention, in the inlet zone of the tubes the temperature rose far quicker and attained very rapidly the temperature at which the catalytic reaction for the formation of ethylene oxide started; thereafter the temperature continued to increase progressively and attained a maximum value of close to 250 °C and then decreased slightly to about 215°C, in particular in the outlet zone of the tubes, which thus made it possible to distance the operating conditions from the maximum flammability zone of the gaseous mixture, and nevertheless gave the catalyst an opportunity to continue to produce ethylene oxide with a good selectivity;
- (b) the selectivity (S) of the reaction to ethylene oxide for a given production (P) of ethylene oxide was, thanks to the process of the invention, higher (curves (1) and (2) of Figure 6) than the selectivity (S) obtained according to a conventional process, all things being equal (curve (3) of Figure 6).